

Magnetic Susceptibility of the Kagome Antiferromagnet $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$

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We analyze the experimental data for the magnetic susceptibility of the material $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ in terms of the Kagome Lattice Heisenberg model (KLHM), discussing possible role of impurity spins, dilution, exchange anisotropy, and both out-of-plane and in-plane Dzyaloshinsky-Moriya (DM) anisotropies, with explicit theoretical calculations using the Numerical Linked Cluster (NLC) method and exact diagonalization (ED). The high-temperature experimental data are well described by the pure Heisenberg model with $J = 170\text{K}$. We show that the sudden upturn in the susceptibility around $T = 75\text{K}$ is due to DM interactions. We also observe that at intermediate temperatures, below $T = J$, our calculated susceptibility for KLHM fits well with a power law $T^{-0.25}$.

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Frustrated magnetic systems represent outstanding challenges in condensed matter physics [1]. While much progress has been made theoretically over the last few decades [2], key issues related to concrete lattice models remain unresolved. Computational methods are restricted to small system sizes or high temperatures, whereas the starting point for field theory methods, which maybe asymptotically exact at low temperatures, involve drastic approximations, which makes their validity for realistic lattice models unclear. Experiments can bridge this gap by providing information all the way from high to low temperatures.

The spin-half Kagome-Lattice Heisenberg Model (KLHM), is one of the best studied frustrated quantum spin models. Much of our knowledge of the system comes from studies of finite-size periodic clusters. Exact Diagonalization studies [3] suggest that the model has a short spin-spin correlation length, and a spin gap of approximately $J/20$. In the finite systems, there are a large number of singlet states below the lowest triplet and their number grows with the system size [4]. Various Resonating Valence Bond (RVB) scenarios have been invoked, and the finite size spectra have also been interpreted to imply deconfined spin-half excitations.

In light of these theoretical results, the experimental behavior of the recently synthesized Kagome-Lattice materials $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ are highly unexpected [5, 6]. The high temperature inverse susceptibility data was found to obey a Curie-Weiss law, with a Curie-Weiss constant of about 300K . Yet, there appears no spin-gap either in the susceptibility or the specific heat or the neutron spectra or in the nuclear spin-lattice relaxation T_1 , down to temperatures below 100mK . At the lowest temperatures the susceptibility saturates and the specific heat shows power-law behavior in temperature. The latter is suppressed by magnetic fields, showing it to be magnetic in origin. A possible interpretation of the substantial rise in susceptibility at low temperatures is that it is due to impurity spins outside the Kagome planes, caused by

substitutions of non-magnetic Zn sites with Cu [7]. However, the fact that the muon shift K tracks the bulk susceptibility χ , implies that the susceptibility is not due to inhomogeneities localized away from the Kagome planes, but rather a bulk behavior of the system.

Here, we use the triangle-based NLC method [8] and ED, to calculate the magnetic susceptibility of the KLHM including various perturbations such as dilution, exchange anisotropy and Dzyaloshinsky-Moriya anisotropy. We find that the high temperature susceptibility is indeed in excellent agreement with that of KLHM. However, the Curie-Weiss fit is fortuitous. The true Curie-Weiss behavior (with $T_{CW} = J$) is only valid for $T > 10J$, a region inaccessible to experiments. When Curie-Weiss fits are made to data for $T < 2J$, the effective Curie-Weiss constant increases in units of J , and hence the true J is smaller than reported in Ref. [5, 6]. The high temperature data fits well with $J = 170\text{K}$.

The sharp upturn in the susceptibility around 75K cannot be accounted for by the KLHM. We find that only a Dzyaloshinsky-Moriya (DM) anisotropy can account for the sharp upturn in the experimental susceptibility. A way to distinguish this from an impurity spin would be by the anisotropy. The excess susceptibility due to DM would be strongly anisotropic, and this anisotropy is temperature dependent.

The NLC method allows us to calculate the susceptibility for the KLHM accurately down to $T = 0.3J$, without extrapolations. In contrast, the high temperature expansions (HTE) fail to converge below $T = J$ [9]. Some extrapolations of NLC and HTE suggest that shortly below $T = 0.3J$, the susceptibility begins to turn down [8, 9]. Unfortunately, these extrapolations to lower temperatures become subjective, and hence we focus only on the region $T > 0.3J$. All NLC calculations reported below are done using the triangle based expansion, where contributions to the thermodynamic system from graphs with complete triangles are included [8]. As appropriate, two highest order calculations are shown.

The Heisenberg Hamiltonian in field h is

$$\mathcal{H} = J \sum_{\langle i,j \rangle} \mathbf{S}_i \mathbf{S}_j - g\mu_B h \sum_i S_i^z. \quad (1)$$

In our calculations we set $J = 1$, Boltzmann constant $k = 1$ and $g\mu_B = 1$. The susceptibility per spin is

$$\chi = \frac{T}{N} \left. \frac{\partial^2 \ln Z}{\partial h^2} \right|_{h=0}, \quad (2)$$

where Z is the partition function. The molar susceptibility, measured experimentally, is related to our susceptibility per spin by the relation, $\chi_{molar} = C\chi$, where the constant $C = N_A g^2 \mu_B^2 / kJ = 0.3752g^2/J$ in cgs units. At high temperatures the susceptibility has a Curie-Weiss form with Curie-Weiss temperature $T_{cw} = J/k$. As discussed by Zheng *et al.* [10], asymptotic Curie-Weiss behavior is only valid for $T \gg J$. At temperatures of order J , one can define an effective temperature dependent Curie-Weiss constant T_{cw}^{eff} as

$$T_{cw}^{eff} = -T - \frac{\chi}{d\chi/dT} \quad (3)$$

If one was to fit χ^{-1} to a linear curve in the vicinity of some temperature T and use the intercept to estimate the Curie-Weiss constant, one would get T_{cw}^{eff} . This quantity for KLHM is shown in Fig. 1. Note that for $T < 2J$ one has $T_{cw}^{eff} \approx 2J$. This means that J for $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ is smaller than estimated in Refs. [5, 6]. In the inset of Fig. 1, we show a comparison of the experimental susceptibility with the theoretical one with $J = 170\text{K}$. The agreement is excellent at high temperatures.

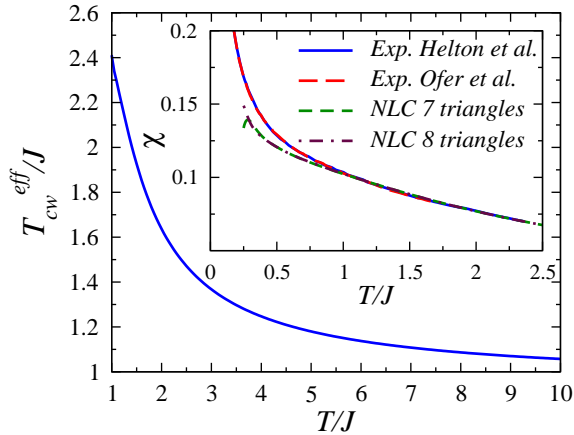


FIG. 1: Temperature dependent effective Curie-Weiss temperature T_{cw}^{eff} for the KLHM. The inset shows fits to the experimental data of Ref. [5, 6]. For both experimental cases we have taken $J = 170\text{K}$. The g -factors needed for the fit are 2.19 for the data from Ref. [5] and 2.33 for the data from Ref. [6]. On the theoretical side, the two highest order NLC results are shown.

While the theoretical susceptibility for the KLHM has a weak upturn at T near $0.3J$, it is inconsistent with

the pronounced rise in the measured susceptibility, which grows significantly below 75K and only saturates to a much higher value at temperatures below 1K . The experimental behavior could arise from several sources. First, there maybe external impurity spins, such as those caused by substitution of Zn sites with Cu [7], which are only very weakly coupled to the electronic spins in the Kagome planes. If present, they would add a Curie like $1/T$ term to the susceptibility at high temperatures. Fig. 2 shows that considering 3 percent impurities allows us to extend the fit down to $T = 0.3J$, but there remains a sharp rise at lower temperatures. A 6 percent impurity concentration eliminates the upturn but makes the data inconsistent with the KLHM. Hence, free impurity spins by themselves, cannot account for the rise in the data. Besides, as argued by Ofer *et al.* [5], in this scenario, it would be difficult to understand why the muon-shift tracks the bulk susceptibility. One would expect local probes to show inhomogeneous behavior and deviate from the bulk averages.

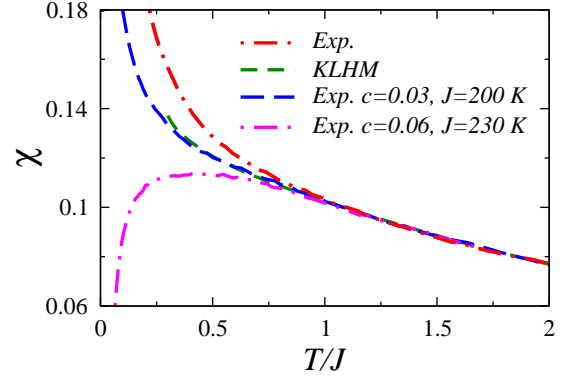


FIG. 2: Comparison of KLHM susceptibility with experimental susceptibility after subtracting Curie contributions from 3 and 6 percent impurities.

A second potential reason for the sudden ferromagnetic behavior could be dilution due to substitution of Cu sites in the Kagome-planes by Zn . The missing spins on the lattice could create local moments in the singlet background and cause a Curie-like susceptibility to arise at low temperatures. They could weakly couple to each other and hence saturate at some much lower temperature. In order to investigate this possibility, we have studied the KLHM with quenched dilution. We assume that at each site, we have a hole with probability c and a spin with probability $1 - c$. The holes are fixed in their position and extensive quantities are averaged over the random configurations C , using the relation

$$\langle O \rangle = \sum_C P(C) O(C) \quad (4)$$

where $P(C)$ is the probability of the configuration C . The susceptibility for several values of hole concentration is shown in Fig. 3. We note that at these intermediate temperatures, holes simply lower the susceptibility

and do not lead to any ferromagnetic tendencies. Thus the static holes do not provide an explanation for the experimental data, either. We have also calculated the susceptibility of KLHM with exchange anisotropy of Ising and XY type. Neither can account for the experimental behavior.

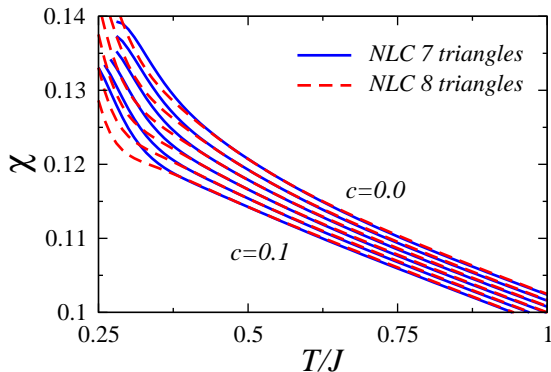


FIG. 3: NLC results for the magnetic susceptibility of the KLHM with hole concentration c ranging from 0 to 10 percent.

We now turn to the Dzyaloshinsky-Moriya (DM) interaction. In Kagome magnets (which we assume lies in the $x-y$ plane), both out of plane (D_z) and in plane (D_p) DM terms are allowed [11, 12].

$$\mathcal{H}_{DM} = \sum_{\langle i,j \rangle} D_z (\mathbf{S}_i \times \mathbf{S}_j)_z + \mathbf{D}_p \cdot (\mathbf{S}_i \times \mathbf{S}_j), \quad (5)$$

The D_z term alternates between the up and down pointing triangles of the Kagome lattice. Its sign can be set by demanding that for the up pointing triangle shown in Fig. 4b, a positive D_z multiplies $(\mathbf{S}_1 \times \mathbf{S}_2)_z$. The in-plane DM term D_p is perpendicular to the bonds and points inward towards the center of the triangles [11, 12]. Since the DM terms break spin rotational symmetry, we need to calculate separately the susceptibility with field along z (χ_z) and in the $x-y$ plane (χ_p). The powder susceptibility χ_a is given by $\chi_a = \frac{1}{3}(2\chi_p + \chi_z)$.

With the DM terms, the different S^z sectors are coupled so we are able to do NLC calculations only up to 6 triangles [8]. Unfortunately, the convergence is poor, and hence we turn to ED of clusters with 12 and 15 sites (with periodic boundary conditions) [9] to study the effects of DM interactions. We find that a pure D_z term suppresses the in-plane and z susceptibilities with respect to KLHM. On the other hand, a pure D_p enhances both in-plane and z susceptibilities with respect to KLHM. Hence, the competition between D_z and D_p can produce varying results. Once $D_p \neq 0$ the sign of D_z is also relevant [13]. In all cases studied, the DM terms produce z susceptibilities which are larger than the in-plane ones.

As long as $D_p > |D_z|$, we find an enhancement of the powder susceptibility with respect to the KLHM. As an example, we show in Figs. 4(a) and 4(b) results for the powder susceptibilities and anisotropy when $D_p = 0.3J$

and $D_z = -0.15J, -0.3J$, respectively. Note that in the theoretical calculations the g -factor is assumed to be isotropic. Since the z -susceptibility rises very rapidly, an anisotropic g -factor enhanced along z will cause an even more rapid rise and will lead to agreement with experiments with a smaller DM anisotropy [14].

Our main point with Fig. 4 is to show that even though more information from the material $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ may be required in order to make a precise estimate of the DM anisotropy, DM interactions are essential to understanding that material. We predict that single crystal measurements should see an upturn in the anisotropy when the powder susceptibility departs from the KLHM result. Such a behavior has already been seen for spin-5/2 Kagome system $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$ [16].

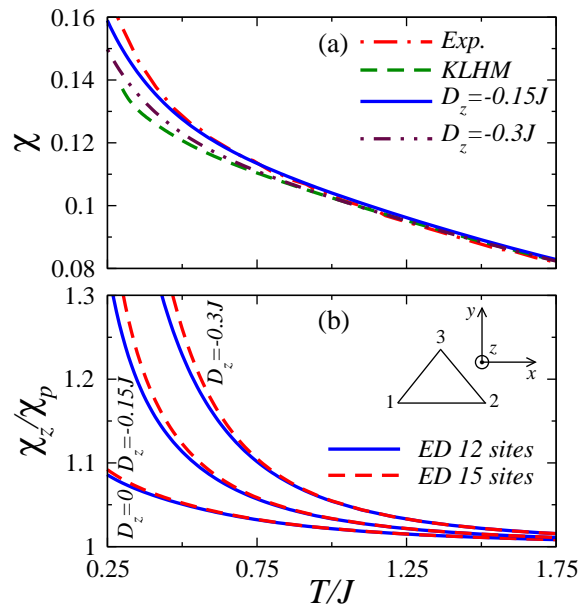


FIG. 4: (a) 15 sites ED calculation of the powder susceptibility with a DM term $D_p = 0.3J$ and different values of D_z , compared with experiments and pure KLHM. (b) Anisotropy vs temperature for $D_p = 0.3J$ and different values of D_z .

Here, we cannot address the measurements at $T \ll J$. An interesting question to ask is whether the lack of spin-gap seen in the experiments is due to DM anisotropy. In magnetically ordered systems, the DM term often creates a spin-gap in the spin-wave spectra. The KLHM is an interesting system where the spin-gap maybe non-zero but singlet excitations maybe gapless [3, 4]. In that case, the DM term can cause the spin-gap to vanish by mixing the singlet states with the spinful states. Alternatively, the experimental data can be interpreted to imply that the KLHM has no spin-gap in the thermodynamic limit.

We now turn our attention back to the pure KLHM. The log-log plot in Fig. 5 makes clear that around $T = J$, where HTE convergence fails, there is a crossover in the temperature dependence of the susceptibility. Below $T = J$, the susceptibility is remarkably well fit by

a power law in temperature of the form $T^{-0.25}$. This non-trivial crossover behavior between the high temperature Curie-Weiss regime and the very low temperature RVB regime deserves further theoretical attention. Experimental measurements of wavevector dependent susceptibilities, at temperatures below J can shed further light on this crossover.

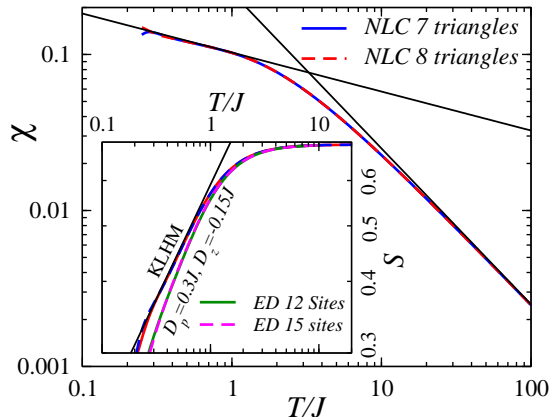


FIG. 5: Log-log plot of the susceptibility of the KLHM. In the inset we show log-log plots of the entropy of the pure KLHM and in the presence of DM terms. Straight lines following the data are $\chi \sim T^{-0.25}$ (low T), $\chi = 1/(4T)$ (high T), and $S \sim T^{0.4}$ (inset).

A rough power law is also seen in the entropy function of the KLHM, which goes as $S \sim T^{0.4}$ (Inset in Fig. 5). This may help explain the failure of naive Pade extrapolations for the specific heat of the KLHM calculated by HTE [9]. It was found that Pade approximations lead to specific heat curves, which when integrated give a finite ground state entropy. It was suggested that this meant the KLHM specific heat has two peaks as a function of temperature as discussed by Elser earlier [17], and HTE simply fails to recover the second peak. However, there is no strong evidence to support the second peak. Our results suggest that instead of a second peak, there maybe a non-trivial power-law regime at low or intermediate temperatures which simple Pade extrapolations of HTE fail to capture. As shown in the inset in Fig. 5, the addition of DM terms to the KLHM produces an increase in the exponent of the entropy from 0.4, bringing it in rather good agreement with low temperature measurements [6]. If the magnetic specific heat for the material $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ can be extracted at higher T , the above issues can be further addressed.

In conclusion, in this paper we have studied the magnetic susceptibility for the material $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ by comparing it with theoretical calculations for KLHM. We find that at high temperatures the susceptibility data is well described by KLHM with $J = 170\text{K}$. The sudden upturn in the experimental susceptibility below $T = 75\text{K}$ is not consistent with KLHM but can be ex-

plained by Dzyaloshinsky-Moriya interactions. Further experiments, can verify or refute the existence of such terms by measuring the anisotropies in the susceptibility. We have also shown that the susceptibility of KLHM has an intermediate temperature regime where χ goes as $T^{-0.25}$. The combined experimental and numerical results raise a fundamental question about whether the KLHM has a spin-gap, or whether it has a gapless spin-liquid ground state [7, 18].

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Note Added.—Recent NMR experiments by Imai *et al.* [19] find that parts of the NMR spectra show a temperature dependence like the bulk susceptibility that grows rapidly as T is lowered while other parts flatten out and then decrease at still lower T . This is exactly what we find for χ_z and χ_p respectively. Thus a simple explanation for these experiments is that they arise from powders oriented perpendicular and parallel to the field.

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